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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 7/2/1997	3. REPORT TYPE AND DATES COVERED Final Technical 09/01/93 - 02/28/97	
4. TITLE AND SUBTITLE Nanoscale Control of Structure in Electrocrystallized Molecular Materials			5. FUNDING NUMBERS N00014-93-1-0946	
6. AUTHOR(S) Michael D. Ward			8. PERFORMING ORGANIZATION REPORT NUMBER 1691-518-6383	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Minnesota Department of Chemical Engineering and Materials Science Amundson Hall 421 Washington Avenue, S. E. Minneapolis, MN 55455			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Navy Office of Naval Research 11SP Attn: AASERT/92 800 North Quincy Street, Arlington, Virginia 22217-5660			11. SUPPLEMENTARY NOTES	
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13. ABSTRACT (Maximum 200 words) The work performed under this AASERT grant augmented our efforts funded by the original parent grant "Electrocrystallization of Molecular Solids" and the recent renewal grant "Electrocrystallization of Nanostructured Molecular Materials" (the AASERT grant overlapped the renewal of the two grants). The intention of the AASERT was to devise approaches to the synthesis and modification of electrocrystallized molecular materials aimed at (1) controlling the supramolecular structure of condensed phases through topological control of molecular networks during crystal growth and (2) nanoscale modification of existing materials using electrochemical atomic force and scanning tunneling microscopies. We have initiated a new discipline that is best described as two-dimensional crystal engineering that uses molecular layer motifs in existing three-dimensional crystal structures as the starting point for the design of organic thin film structures.				
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FORM A2-2

AUGMENTATION AWARDS FOR SCIENCE & ENGINEERING RESEARCH TRAINING (AASERT)
REPORTING FORM

The Department of Defense (DOD) requires certain information to evaluate the effectiveness of the AASERT program. By accepting this Grant Modification, which bestows the AASERT funds, the Grantee agrees to provide the information requested below to the Government's technical point of contact by each annual anniversary of the AASERT award date.

1. Grantee identification data: (R & T and Grant numbers found on Page 1 of Grant)

- a. University of Minnesota, CEMS Department
University Name
- b. N00014-93-1-0946
Grant Number
- c. _____
R & T Number
- d. Michael D. Ward
P.I. Name
- e. From: 09/01/93 To: 02/28/97
AASERT Reporting Period

NOTE: Grant to which AASERT award is attached is referred to hereafter as "Parent Agreement."

2. Total funding of the Parent Agreement and the number of full-time equivalent graduate students (FTEGS) supported by the Parent Agreement during the 12-month period prior to the AASERT award date.

- a. Funding: \$ 100,000
- b. Number FTEGS: 2

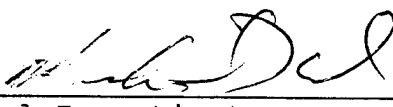
3. Total funding of the Parent Agreement and the number of FTEGS supported by the Parent Agreement during the current 12-month reporting period.

- a. Funding: \$ 100,000
- b. Number FTEGS: 2

4. Total AASERT funding and the number of FTEGS and undergraduate students (UGS) supported by AASERT funds during the current 12-month reporting period.

- a. Funding: \$ 37,000
- b. Number FTEGS: 1
- c. Number UGS: 0

VERIFICATION STATEMENT: I hereby verify that all students supported by the AASERT award are U.S. citizens.


Principal Investigator

7/7/97
Date

OFFICE OF NAVAL RESEARCH

FINAL TECHNICAL REPORT

for

ASSERT GRANT # N00014-93-1-0946
(augmentation for parent grant N00014-93-1-0563)

"Nanoscale Control of Structure in Electrocrystallized Molecular Materials"

Michael D. Ward

Department of Chemical Engineering and Materials Science
University of Minnesota

Amundson Hall
421 Washington Ave. SE
Minneapolis, MN 55455

June 23, 1997

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OFFICE OR NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT (Part I)

PR Number: 96PR0-1034 (for parent grant N00014-93-1-0563)

Contract/Grant Number: N00014-93-1-0946

Contract/Grant Title: Nanoscale Control of Structure in Electrocrystallized Molecular Materials

Principal Investigator: Michael D. Ward

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- a. Number of papers submitted to refereed journals, but not published: 5
- b. + Number of papers published in refereed journals: 2
- c. + Number of books or chapters submitted, but not yet published: 1
- d. + Number of books or chapters published: 1
- e. + Number of printed technical reports/non refereed papers: 4
- f. + Number of patents filed: 0
- g. + Number of patents granted: 0
- h. + Number of invited presentations: 16
- I. + Number of submitted presentations 0
- j. + Honors/Awards/Prizes for contract/grant employees (list attached): 4
- k. Total Number of Full-Time Equivalent Graduate Students and Post-Doctoral Associates
Supported on this Project Number

Graduate Students	1
Postdoctoral Associates	0

Female Graduate Students	1
Female Post-Doctoral Associates	0

Minority Graduate Students	0
Minority Post-Doctoral Associates	0

Asian Graduate Students	0
Asian Post-Doctoral Associates	0

1. Other Funding

<u>Agency (Period)</u>	<u>Title</u>	<u>\$ This year</u>	<u>\$ Total</u>
*National Science Foundation (8/1/94-7/31/97)	Directing Growth of Molecular Crystals on Monolayers	\$110,000	\$350,000
E. I. duPont (1997-98)	Educational Gift (educational gift)	\$20,000	
NSF/ERC Center for Interfacial Engineering University of Minnesota (9/15/92-present)	Crystallization of Organic Crystals in Nanodomains of Block Copolymers	1 student (co-advised)	1 student (co-advised)
NSF/ERC Center for Interfacial Engineering University of Minnesota (9/15/94-present)	Crystallization of Molecular Dyes in Confined Media	1 student	1 student
NSF/ERC Center for Interfacial Engineering University of Minnesota (9/15/95-present)	Elucidating the role of Hydrogen Bonding in Cell Adhesion	1 student (co-advised)	1 student (co-advised)
NSF/ERC Center for Interfacial Engineering University of Minnesota (9/15/96-present)	Tandem Self-Assembled Membranes from Molecular Networks and Block Copolymers	1 student (co-advised)	1 student (co-advised)
NSF/ARI	Renovation of Amundson Hall	\$327,000	Granted October 1996
NSF/IMR	Wide-angle diffraction system	\$138,200	Granted July 1996

Citation list

a. Papers submitted to refereed journals, but not published (related to this AASERT grant)

- ☐ Epitaxially-Driven Assembly of Crystalline Molecular Films on Ordered Substrates, Julie A. Last, Andrew C. Hillier, Daniel Hooks, Jeffrey B. Maxson, and Michael D. Ward, submitted.

b. Papers Published in Refereed Journals (related to this AASERT grant)

- ☐ Organic Crystal Surfaces: Structure, Properties and Reactivity, M. D. Ward, *Current Opinion in Colloid and Interfacial Science*, **1997**, 2, 51.
- ☐ Frictional Anisotropy and Electrochemical Annealing of Conducting Molecular Films, J. A. Last and M. D. Ward, *Adv. Mater.*, **1996**, 8, 730.
- ☐ Epitaxial Overlayer-Substrate Interactions for Organic Thin Films and Crystals, A. C. Hillier and M. D. Ward, *Phys Rev. B*, **1996**, 54, 14037.

c. Books or Chapters Submitted but not yet Published (related to this AASERT grant)

- ☐ None

d. Books or Chapters Published (related to this AASERT grant)

- ☐ Scanning Tunneling and Atomic Force Microscopy of Electrochemical Interfaces (Invited Book Chapter), M. D. Ward and H. S. White, *Modern Techniques in Electroanalysis*, Petr Vanysek, Ed.; Volume 139, Wiley (New York), 1996, p 107.
- ☐ "Molecular Engineering of Crystals by Electrostatic Templating," P. J. Fagan and M. D. Ward, in *Perspectives in Supramolecular Chemistry: The Crystal as a Supramolecular Entity*, G. R. Desiraju, Ed., Wiley, New York, 1996.

e. Printed Technical Reports/Non-Refereed Papers (related to this AASERT grant)

- (9) Electrochemical Annealing and Friction Anisotropy of Domains in Epitaxial Molecular Films
- (12) Epitaxial Interactions Between Molecular Overlayers and Ordered Substrates

f. Patents Filed

None

g. Patents Granted

None

h. Invited Presentations

- ☐ European Conference on Molecular Electronic Materials, August 26 - 31, 1995, Mittelberg, Austria, Electrochemical Growth of Crystalline Organic Conductors: The Influence of Epitaxy and Commensurism on Film Properties

- ☐ NATO Advanced Research Workshop on Modular Chemistry, September 9 - 12, 1995 Estes Park, Colorado, "Nucleation and Growth of Crystalline Organic Materials: Epitaxy and Visualization at that Nanoscale."
- ☐ NATO Advanced Research Workshop on Modular Chemistry, September 9 - 12, 1995 Estes Park, Colorado, "Modular Control of Crystal Architecture with Two-Dimensional Hydrogen-Bonded Assemblies."
- ☐ Universite Catholique, Louvain-la-Neuve, Belgium, October 10, 1995, "Nucleation and Growth of Crystalline Organic Materials: Epitaxy and Visualization at that Nanoscale"
- ☐ Universite Louis Pasteur, Strasbourg, France, September 27, 1995, "Nucleation and Growth of Crystalline Organic Materials: Epitaxy and Visualization at that Nanoscale"
- ☐ University of Stuttgart, Stuttgart, Germany, October 18, 1995, "Nucleation and Growth of Crystalline Organic Materials: Epitaxy and Visualization at that Nanoscale"
- ☐ Universite Louis Pasteur, Strasbourg, France, November 10, 1995, "Modular Control of Crystal Architecture with Two-Dimensional Hydrogen-Bonded Assemblies"
- ☐ Institute Charles Sadron, Strasbourg, France, November 14, 1995, "Nucleation and Growth of Crystalline Organic Materials: Epitaxy and Visualization at that Nanoscale"
- ☐ MPI, Mainz, Germany, November 21, 1995, "Nucleation and Growth of Crystalline Organic Materials: Epitaxy and Visualization at that Nanoscale"
- ☐ MPI, Mainz, Germany, November 21, 1995, "Modular Control of Crystal Architecture with Two-Dimensional Hydrogen-Bonded Assemblies"
- ☐ Universite Louis Pasteur, Strasbourg, France, December 6, 1995, "Structure and Symmetry in Condensed Matter: Common Features in Organic Crystals, Polymers and Surfactants"
- ☐ California Institute of Technology, Pasadena, CA, January 29, 1996, "Nucleation and Growth of Crystalline Organic Materials: Epitaxy and Visualization at that Nanoscale"
- ☐ University of California at Irvine, January 30, 1996, "Nucleation and Growth of Crystalline Organic Materials: Epitaxy and Visualization at that Nanoscale"
- ☐ Pennsylvania State University, State College, PA, February 6, 1996, "Nucleation and Growth of Crystalline Organic Materials: Epitaxy and Visualization at that Nanoscale"
- ☐ Lehigh University, Bethlehem, PA, February 7, 1996, "Nucleation and Growth of Crystalline Organic Materials: Epitaxy and Visualization at that Nanoscale"
- ☐ University of Pennsylvania, Philadelphia, PA, February 12, 1996, "Quartz Crystal Microbalance: Principles and Methods"
- ☐ E.I. duPont de Nemours, Central Research and Development, April 23, 1996, "Modular Control of Crystal Architecture with Two-Dimensional Hydrogen-Bonded Assemblies"
- ☐ MRS meeting, Boston, MA, December 2, 1996, "Heteroepitaxial Growth of Molecular Films"
- ☐ University of California at Santa Barbara, January 14, 1997, "Nanoporous Molecular Sandwiches" Pillared Two-Dimensional Hydrogen-Bonded Networks with Adjustable Porosity"

- Universite' Louis Pasteur, March 27, 1997, "Self-Assembly of Crystalline Organic Materials: Epitaxy and Visualization at that Nanoscale"
- Americal Chemical Society Symposium on Materials Chemistry, San Francisco, April 15, 1997, "Nanoporous Molecular Sandwiches" Pillared Two-Dimensional Hydrogen-Bonded Networks with Adjustable Porosity"

i. Submitted Presentations

j. Honors/Awards/Prizes

Editorial Advisory Board, *Supramolecular Science* (M. D. Ward)
Editorial Advisory Board, *Chemistry of Materials* (M. D. Ward)
Amundson Fellowship (M. D. Ward)
Visiting Scientist, Universite' Louis Pasteur, Strashourg, FRANCE

Project Summary

a. Principal Investigator: Michael D. Ward

b. Current Telephone Number: (612) 625-3062

c. Cognizant ONR Scientific Officer: Robert J. Nowak (current temporary office: Ron DeMarco)

d. Brief Description of Project

The work performed under this AASERT grant augmented our efforts funded by the original parent grant "Electrocrystallization of Molecular Solids" and the recent renewal grant "Electrocrystallization of Nanostructured Molecular Materials" (the AASERT grant overlapped the renewal the two grants). The intention of the AASERT was to devise approaches to the synthesis and modification of electrocrystallized molecular materials aimed at (1) controlling the supramolecular structure of condensed phases through topological control of molecular networks during crystal growth and (2) nanoscale modification of existing materials using electrochemical atomic force and scanning tunneling microscopies. This work has augmented studies in the parent proposal that are aimed toward elucidating the microscopic origins for molecular assembly on substrates for crystalline phases that can be grown electrochemically. We have discovered that three-dimensional bulk crystals which have layered structures can be used as a starting point for the design of thin films with functional properties. While our intention was to advance this to the stage where ultrasmall "molecular devices" could be made, for example, heterostructures composed of different crystalline phases with semiconducting properties, we have spent considerable effort elucidated the influence of epitaxy on the formation of these films. This has resulted in new models for epitaxy that describe the stabilization of van der Waals films on ordered substrates, systems for which the energetics are quite subtle and commensurism typically is impossible. Our group, including the student funded by the AASERT grant, has advanced the concept of coincident epitaxy for these organic thin films. This has included the development of efficient computer algorithms that enable prediction of new thin film/substrate structures while also enabling rationalization of experimentally observed structures. This work has combined electrochemistry, interfacial science and crystal engineering. Essentially, we have initiated a new discipline that is best described and two-dimensional crystal engineering that uses molecular layer motifs in existing three-dimensional crystal structures as the starting point for the design of organic thin film structures. This was a necessary first step in a plan to develop device structures based on molecular materials. The work also has contributed substantially to our knowledge of nanoscale processing under ambient conditions, a considerable advantage over more expensive routes to thin films (such as molecular beam epitaxy). A key contribution by the student funded by the AASERT grant is the demonstration that, given two possible coincident configurations for a molecular overlayer on a substrate, the configuration observed is that which has the smallest supercell. Energy calculations confirm that this is due to a lesser number of energetically unfavorable non-commensurate overlayer sites. A full paper on this topic has been submitted, and a technical report will follow.

Recently, the student funded the AASERT grant also contributed to the discovery of spatially controlled electrochemically induced etching of metal chalcogenide surfaces, which was observed directly by AFM. This etching was achieved with a gold-coated AFM tip which served as a counterelectrode to the biased metal chalcogenide surface. When the AFM tip was held close to the surface etching occurred in a very small region below the tip. This will enable us to study the growth of organic thin films in nanoscale features on the metal chalcogenide surface, complementing similar studies on thermally etched graphite surfaces (which have nanoscale etch pits, but without spatial control). This work is being performed under the parent grant and a recently awarded AASERT grant.

e. Summary of Significant Results from the AASERT Grant

- Advancement of atomic force microscopy (AFM) methods for *in situ*, real-time examination of electrochemical nucleation and growth of molecular films, nanostructures and bulk crystals solids in solvent media
- Advanced epitaxial principles that relate the symmetry and structure of a substrate to:
 - the normal and azimuthal orientation of nuclei and molecular overlayers
 - the orientation and size of bulk crystals grown from these overlayers nuclei
 - the molecular order and lattice constants of molecular overlayers
 - stresses and defects induced by epitaxy with the substrate
- Developed a new analytical model of heteroepitaxial interfaces that enables rapid and computationally efficient analysis of an overlayer-substrate interface. The type of epitaxy, i.e., coincident vs. commensurate, the azimuthal relationship, and the degree of epitaxy can be determined. We have demonstrated that this analytical model provides solutions identical to those realized by total potential energy calculation. However, the analytical model provides these solutions in less than 1% of the time required for total potential calculations. This also enables searches for epitaxial reconstructed overlayer lattices. The applicability of this approach has been demonstrated for electrochemically grown overlayers reported by our laboratory as well as organic overlayers produced in other laboratories by molecular-beam epitaxy.
- We have demonstrated "electrochemical annealing" of domain boundary defects in an epitaxial crystalline monolayer whose structure mimics the (001) layers of the organic superconductor β -bis(ethylenedithio)tetrathiafulvalene triiodide, $(\text{ET})_2\text{I}_3$, has been visualized *in situ* using real-time atomic force microscopy (AFM). These defects can be observed readily by lateral force imaging, and high resolution imaging reveals that the domains are oriented azimuthally at angles of $\pm n60^\circ$ because of coincident epitaxy with the HOPG substrate. The surfaces of differently oriented domains in a single AFM image exhibited different degrees of friction at a fixed scan direction due to the molecular anisotropy of the monolayer surface, which causes the tip to experience differently oriented molecular fields on these domains. The ability to detect this friction anisotropy is a direct consequence of the crystalline order of the rigid monolayer. Potential cycling about the deposition potential resulted in a reduction in the number and size of domains, with smaller domains eventually adopting the orientation of surrounding larger ones, ultimately forming large ($> 15 \mu\text{m}^2$) defect-free monolayers. This demonstrates that the defect density of redox-active molecular films can be reduced by relatively simple means.
- We demonstrated that, given two possible coincident configurations for a molecular overlayer on a substrate, the configuration observed is that which has the smallest supercell. Energy calculations confirm that this is due to a lesser number of energetically unfavorable non-commensurate overlayer sites.

These studies are providing elucidation of the crucial factors in the growth of conducting and superconducting organic thin films, nanostructures and bulk crystals. The understanding gained will provide the foundation for fabricating heteroepitaxial thin films with molecular dimensions that may have novel electronic properties. Furthermore, we are elucidating the relationship between substrate-overlayer epitaxy, overlayer elastic properties, interfacial stresses and film quality, which is applicable to the growth of ultrathin organic films which is not only germane to the properties of conducting thin films, but also those being explored for their unique optical properties (e.g.; photodetectors, non-linear optical materials). However, our electrochemical approaches allow for fine control of the nucleation and growth rates and direct observation of overlayer and nuclei formation, while enabling deposition on substrates with unusual geometries (contrary to vapor deposition methods). Our studies also provide much needed insight into the atomic/molecular level events involved in electrodeposition, which is needed if further advances in the electrochemical fabrication of device structures are to be made.